

FWP KCC053 Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

**Synopsis:** The application of the phosphate-based supports open up a new avenue in the search for highly active, stable, and selective gold catalysts for CO oxidation. The unique structure features of phosphates, non-oxide support, shed new light on the mechanism associated with gold based catalysis. The reaction of CO with gas phase oxygen is delayed by reduction of cationic Au to metallic Au by CO at RT. An unexpected Au-assisted storage of active oxygen provides new pathway for CO oxidation at RT over Au/FePO<sub>4</sub>, suggesting there are two channels for CO oxidation on this catalyst.

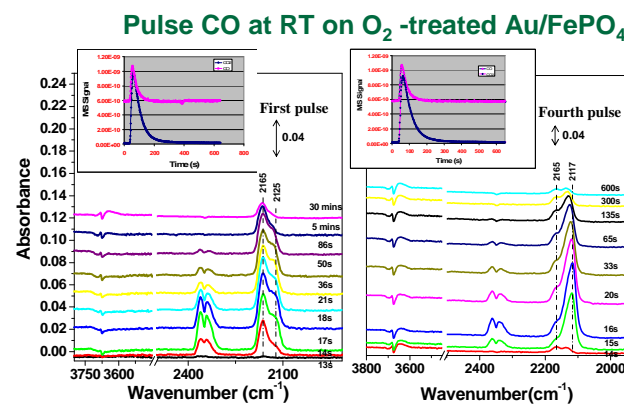
## Introduction and Objective

- Much of work focused on oxides supported Au catalysts has been based upon characterization of the structure and oxidation state of the Au particles, the effect of particle size on activity, the activation of CO and O<sub>2</sub> on Au particles.
- Only few investigations on the catalytic properties and characterization of gold on non-oxide supports.
- A new non-oxide support system based on metal phosphates has been developed for Au catalysts used in CO oxidation.
- The objective of this work is to clarify the mechanisms for CO oxidation over metal phosphates supported Au catalysts.**

## Experiments

- Approach: Operando DRIFTS-QMS**  
A Fourier transform Infra-red (FTIR) spectrometer is coupled with a down-stream quadrupole mass spectrometric (QMS) gas sampling system for simultaneously monitoring surface chemical species and gas phase products analysis.
- Pretreatment: 5.5 wt% Au/FePO<sub>4</sub>**  
Calcination: 200 °C in O<sub>2</sub> for 2 h --- O<sub>2</sub>-treated sample  
Reduction: 200 °C in O<sub>2</sub> for 2 h then in H<sub>2</sub> (CO) for 2 h --- H<sub>2</sub> (CO)-treated sample
- Raman spectroscopy:**  
Raman spectra were collected at room temperature after different pretreatments on a triple-stage spectrometer with laser excitation at 325 nm.

## Results



- Two kinds of cationic gold (Au<sup>d+</sup>, 0 < d ≤ 1)  
2165cm<sup>-1</sup>: strongly adsorbs CO, and hard to reduce by CO  
~ 2125cm<sup>-1</sup>: weakly adsorbs CO, and easy to reduce by CO
- Au/FePO<sub>4</sub> catalyst could strongly adsorb or store O<sub>2</sub>

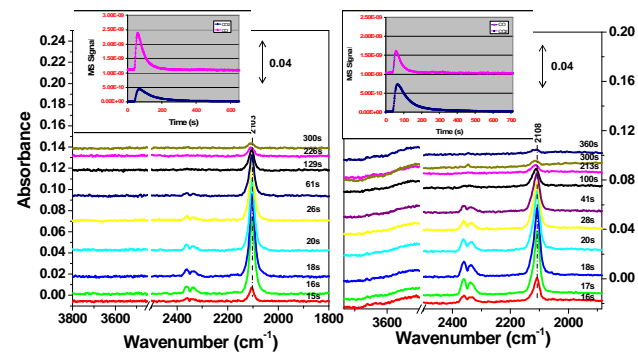
Is the active structural O in Au/FePO<sub>4</sub> related with Au or not?

- No CO adsorption and CO<sub>2</sub> formation on FePO<sub>4</sub> alone
- O<sub>2</sub> chemisorptions results:  
Au/FePO<sub>4</sub>: 32 micromole/gram  
Au/Fe<sub>2</sub>O<sub>7</sub>: 3200 micromole/gram, supposing Au/FePO<sub>4</sub> all reduced to Au/Fe<sub>2</sub>O<sub>7</sub> by H<sub>2</sub>
- FePO<sub>4</sub>: no O<sub>2</sub> chemisorption at RT

**Au must be present for surface reduction of FePO<sub>4</sub> to occur at RT**

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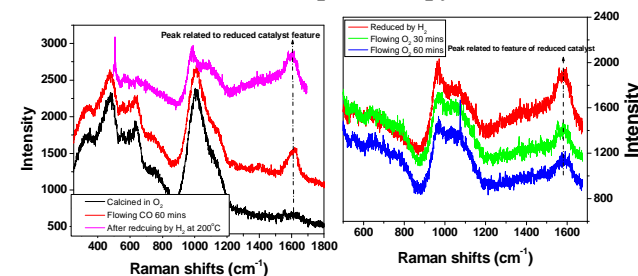
## Pulse CO at RT on H<sub>2</sub>-treated Au/FePO<sub>4</sub>



- Only metallic gold existed after catalyst treated in H<sub>2</sub>
- Small amount of stored active O<sub>2</sub> is still available
- The active O could replenished by flowing O<sub>2</sub> to reduced Au/FePO<sub>4</sub> catalyst at RT

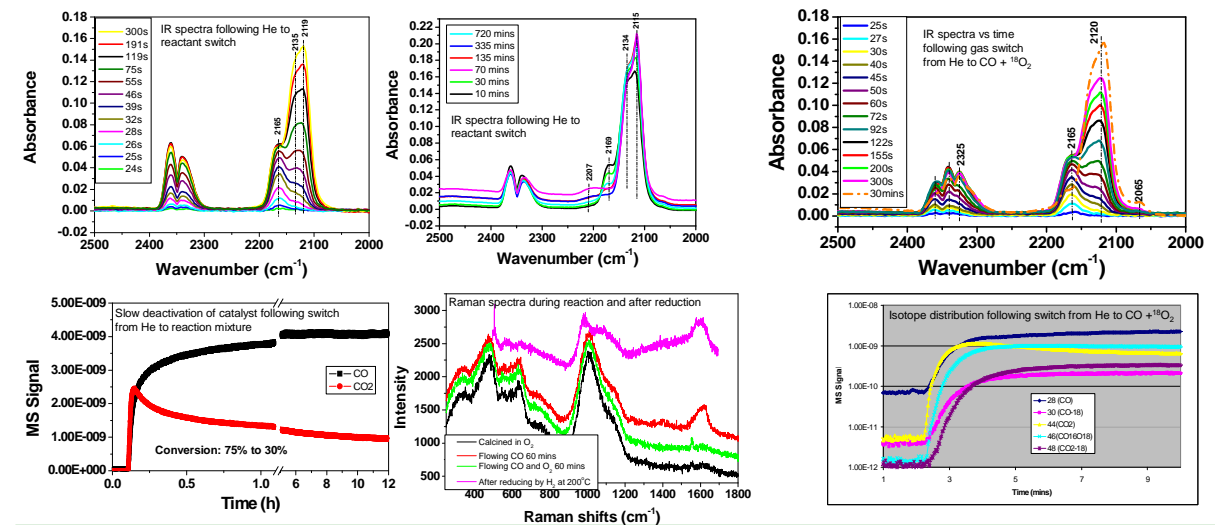
Adsorbed O<sub>2</sub> or structural O of FePO<sub>4</sub>?

Raman spectroscopy



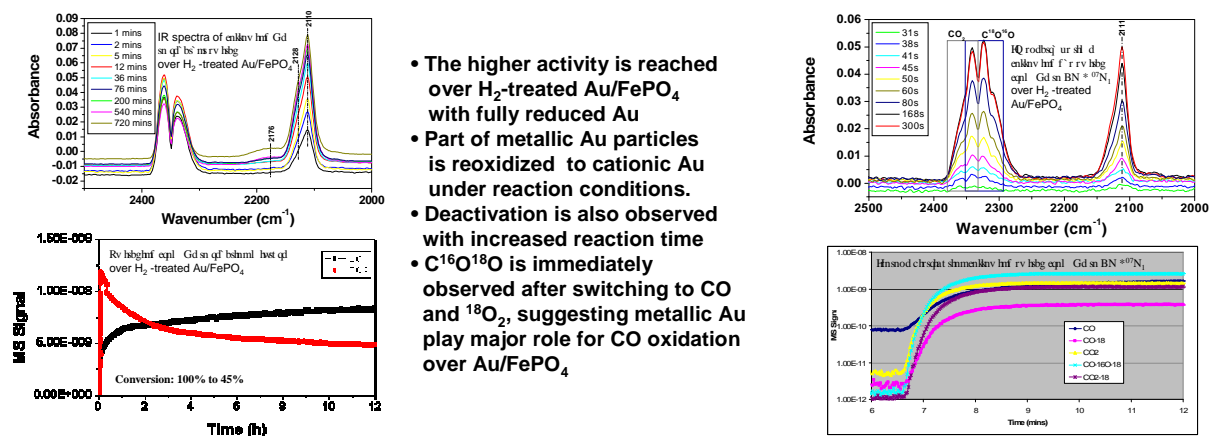
The active form of O from Au/FePO<sub>4</sub> catalyst is **structural O of FePO<sub>4</sub>**.

## CO oxidation proceeds through two channels over O<sub>2</sub> pre-treated Au/FePO<sub>4</sub>



- Cationic Au can't be completely reduced to metallic Au, and higher oxidation state of Au formed after long time reaction
- CO oxidation by <sup>18</sup>O<sub>2</sub> is delayed on the Au surface by reduction of cationic Au with CO in reaction conditions
- Au-assisted storage of active oxygen provides new pathway for CO oxidation at RT over Au/FePO<sub>4</sub>, which suggests there are two channels to proceed CO oxidation
- Deactivation is observed with reaction time increasing

## Metallic Au plays a major role on CO oxidation over Au/FePO<sub>4</sub>



- The higher activity is reached over H<sub>2</sub>-treated Au/FePO<sub>4</sub> with fully reduced Au
- Part of metallic Au particles is reoxidized to cationic Au under reaction conditions.
- Deactivation is also observed with increased reaction time
- C<sup>16</sup>O<sup>18</sup>O is immediately observed after switching to CO and <sup>18</sup>O<sub>2</sub>, suggesting metallic Au play major role for CO oxidation over Au/FePO<sub>4</sub>

## Summary

**Au/FePO<sub>4</sub> catalyst:**

- Cationic gold is dominant on Au/FePO<sub>4</sub> after pretreatment in O<sub>2</sub> at 200°C, and part of cationic Au could be reduced to metallic Au by CO at RT
- Unexpected Au-assisted surface redox property provides new pathway for CO oxidation at RT
- Metallic Au plays major role for CO oxidation over Au/FePO<sub>4</sub>

**CO oxidation proceeds through two channels over Au/FePO<sub>4</sub>:**

- CO directly react with activated O<sub>2</sub> on Au surface
- CO reacts with structural O of FePO<sub>4</sub> via Mars-van Krevelan mechanism, i.e., gas phase O<sub>2</sub> re-supplies the structural O to the FePO<sub>4</sub>.